

Investigation of the Tar By-Product
Of the Water Gas Industry

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An investigation of the tar
by-product of the water gas

A THESIS

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PRESENTED TO THE PRESIDENT AND FACULTY

OF

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IN

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SUBMITTED BY

Robert E. Harper and Ralph H. Fash.

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Accepted.

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AN INVESTIGATION

OF

THE TAR BY-PRODUCT OF THE WATER GAS INDUSTRY.

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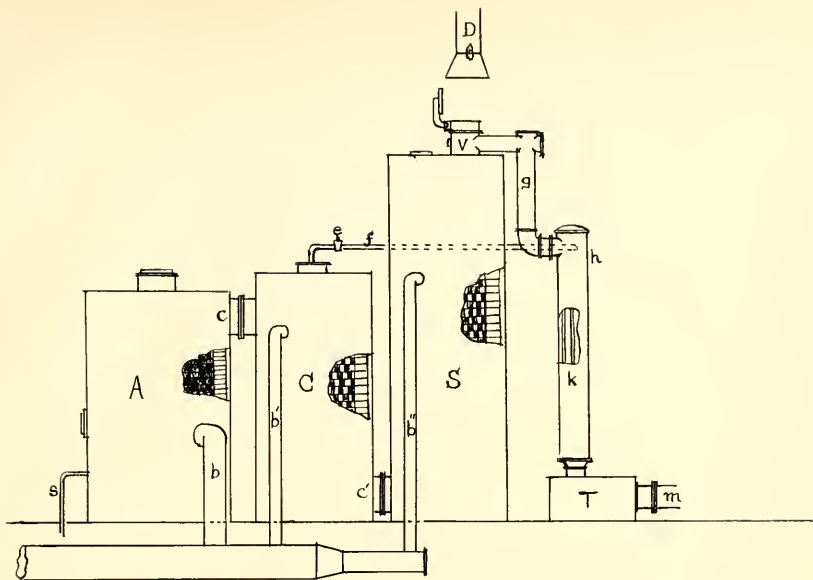
By Robert B. Harper and Ralph H. Fash.

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use of the by-product, coal tar, is brought out clearly in the U. S. Geological Survey Report on the Mineral Resources of the United States for 1903. According to the report, we produced in 1903, 62,964,393. gallons of coal tar. The value of the coal tar produced in that year was \$2,199,969. while the value of the imports of chemicals obtained from coal tar for the fiscal year ending June 30th, 1903, was \$7,690,885. with a duty of \$1,692,445. making a total of \$9,383,330. The report in conclusion states, that, "A conservative estimate would place the total value of these products in the wholesale markets of this country in both 1902 and 1903 at \$12,000,000." From the foregoing statistics, we can readily see how profitable to other nations is our wastefulness of valuable by-products.

Coal tar constituents and products have been the subjects of investigation and study for years, but water gas tar possibilities seem to have been somewhat overlooked or deemed unimportant by those in the field of research. On this account, an investigation, if it is worthy of being considered such, of water gas tar appeared to be the more attractive problem of the two, and hence was undertaken with the hope of enlarging its field of usefulness.

It may be well to explain, briefly, how water gas is manufactured and at what stage of the process we obtain the tar by-product which is the subject of the present investigation. The following diagram will aid in explaining the process.



IMPROVED LOWE CARBURETTED WATER GAS PLANT.

A, Generator; b, b', b'', blast pipes; c, pipe leading to carburettor from generator; C, carburettor; c', pipe leading to superheater; S, superheater; V, stack valve; D, hood for stack valve; e, tap on oil pipe; f, oil pipe; g, h, mixed gas pipes; k, oil heater; T, seal; n, pipe leading to purifying plant; s, steam supply pipe.

An outline of the process as used in a plant of the above description would be, roughly, as follows:-

Air at about 13 inches of water pressure would be admitted to the bottom of the generator by the blast pipe, b, and, passing through the fuel, would form producer gas, and the reaction being exothermic, the temperature of the fuel will gradually rise. The producer gas passes out of the generator by the pipe, c, into

the carburettor, C, where it meets a blast of air from the pipe, b', and is partially consumed, the heat of combustion raising the temperature of the chequer bricks in the vessel. The unconsumed gas and the products of combustion of the consumed gas pass by the pipe, c', into the superheater, S, where a further blast of air enters by the pipe, b'', and completely consumes the producer gas, raising by the combustion the temperature of the chequer bricks in the vessel. The products of combustion pass out at the open stack valve, V, and up the shaft, D. When this process has continued for five to ten minutes, according to the heat of the fuel and of the vessels at the commencement, and the fuel in the generator is at a bright heat of about $1,100^{\circ}\text{C}.$, steam is admitted instead of air to the generator by the pipe, s, and the blast is shut off from the other vessels, and the stack valve, V, closed. Water gas is formed in the generator, A, and passes into the carburettor, C. At the same time the tap, e, on the oil pipe, f, is turned on, and heated oil slowly pumped into the carburettor. The water gas meets the spray of oil, which is gradually gasified, and carried on by the stream of water gas into the superheater, S, where it is converted into a permanent gas, and the mixed oil and water gas leaving this vessel has a fairly uniform composition. The mixed gas passes by the pipes, g and h, the latter of which contains the oil heater, k, into the seal, T, the pipe, h, dipping under the tar in the bottom of the vessel.

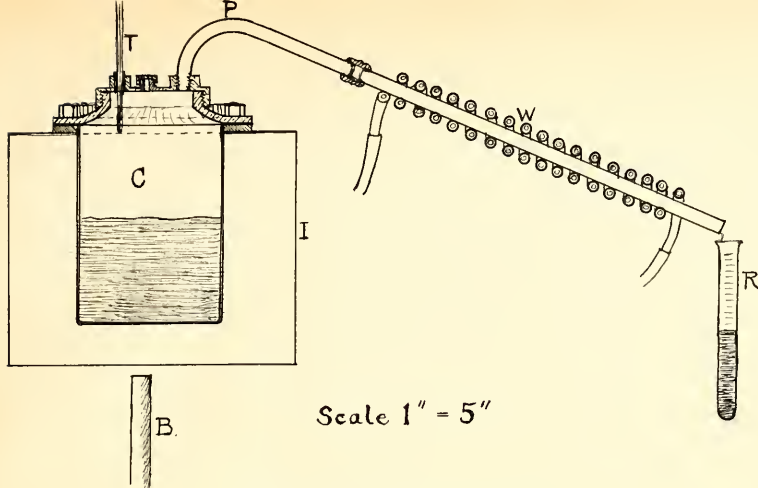
As will be seen from the description of the process, most of the tar formed collects in the seal, T. The tar is drawn off from the seal, T, into storage tanks.

At the gas works from which the samples of tar were taken, the water gas was produced by a process very similar to the one just described. In this plant, about 175 gallons of crude petroleum is used to a ton of coke. From each ton of coke about 15,000 cubic feet of gas is obtained and about $3/4$ gallons of water gas tar is deposited with the production of every thousand cubic feet of gas. Thus we get from 10 to 12 gallons of tar deposited for every charge of 1 ton of coke and 175 gallons of petroleum.

In order to have a fairly uniform and representative sample of water gas tar for the purpose of investigation, about 10 gallons was drawn off from one of the storage tanks of the Universal Gas Company's works located at 31st St. and Archer Ave., Chicago, Ill.

The tar was a thin black liquid having a specific gravity of 1.1070 at 20°C. Its odor was distinctively that of water gas with which it seemed to be thoroughly saturated.

The first distillation of a litre sample was carried out in a copper retort such as is shown in the following figure;-



DISTILLATION APPARATUS.

C, Copper retort; T, thermometer; P, distillation pipe; W, lead worm carrying cooling water; R, graduated receiver of distillate; I, iron hood for uniform heating; B, Bunsen burner for heating.

Three distinct distillations of one litre samples were made in order that the resulting fractions might give a mean or average of the different results obtained due to variable rates of heating.

The first drops of distillate came over at about 93°C . and at 98°C . much "rattling" was heard inside of the retort. This was followed by an overflow of the tar at the latter temperature, although the crude tar barely filled one-half of the retort at the beginning of the distillation. By careful and slow heating, the amount of the overflowing tar could be minimized. However, several methods of overcoming this difficulty were tried, but none of them met with success. A distillation with 3 per cent of calcium chloride seemed to retard the tendency of the tar to foam over until a

temperature of 100°C . had been reached, when the tar came over in quantity as in the first case. A vacuum distillation was made under a vacuum of 25 inches of mercury which was maintained by means of an oil pump. This attempt was not productive of good results, as at 63°C . nearly $3/4$ of the original charge of crude tar came over within a minute under slow heating. The only remedy for the prevention of the foaming over of the crude tar seemed to be a very slow heating of the cold charge. With the retort half full of the crude tar, it required from three to four hours to heat the mixture from 20°C . to 100°C . and to minimize the amount of tar mechanically carried over.

In the three copper retort distillations, fractions were taken over a range of 10°C . from 90°C . up to 460°C . The water which was distilled over, was mechanically removed from the oils in order to facilitate fractional distillation. The fractions, from the three retort distillations, taken through like ranges of temperature were added together and subjected to 3 fractional distillations. It was impossible to further purify and separate the constituents of the various fractions owing to the short time allotted for the investigation. The final fractions from the third fractional distillation cover a range of 5°C . from 70°C . to 460°C . as observed on the thermometer.

The following table shows the results obtained under a retort distillation at atmospheric pressure:-

A TABLE SHOWING

AVERAGE RESULTS OF THREE COPPER RETORT DISTILLATIONS.

-:-

Fraction. °C.	Percent.	Characteristics of distillate.	Remarks.
90-100.	6.05	Water.	
	8.95	Crude tar and some light oils.	
100-110.	1.55	Water.	
	.27	Brown oil and some tar.	Color of oils up to 160°C. due to tar in the distil- lation pipe.
110-120.	.18	Water.	
	.08	Brown oil.	
120-130.	.15	Water.	
	.11	Brown oil.	"
130-140.	.15	Water.	
	.09	Brown oil.	"
140-150.	.07	Water.	
	.08	Brown oil.	"
150-160.	.06	Water.	
	.11	Deep red-brown oil.	"
160-170.	.04	Light brown oil.	"
170-180.	.07	Yellow oil.	
180-190.	.06	Yellow oil.	
190-200.	.07	Yellow oil.	
200-210.	.13	Yellow oil.	
210-220.	1.07	Yellow oil.	
220-230.	.50	Yellow oil.	
	1.33	White crystalline solid.	Darkens on exposure to air.
230-240.	.03	Yellow oil.	
	2.30	Fine white crystals.	

Fraction. °C.	Percent.	Characteristics of distillate.	Remarks.
240-250..	.03 3.50	Yellow oil.	
250-260.	.20 2.82	Yellow oil. Amorphous white solid.	
260-270.	.65 1.63	Golden yellow oil. Amorphous white solid.	
270-280.	1.63 .03	Golden yellow oil. Amorphous white solid.	Oils above 270° darken after sever- al days ex- posure to air.
280-290.	2.33	Golden yellow oil.	
290-300.	2.03	Golden yellow oil.	
300-310.	1.90 .13	Golden yellow oil. Light yellow solid.	
310-320.	1.67 .38	Golden yellow oil. Light yellow solid.	
320-330.	1.42 .75	Light brown oil. Yellow solid.	
330-340.	.77 .88	Light brown oil. Yellow solid.	
340-350.	.23 1.08	Light brown oil. Yellow solid.	
350-360.	.28 1.98	Light brown oil. Deep yellow crystalline solid.	
360-370.	.08 .35 1.47	Red brown oil with bloom. Brown oil. Reddish yellow solid.	
370-390	.87 .03 1.30	Deep red brown oil with bloom. Red brown oil. Orange colored solid.	
390-410.	.47 2.50	Reddish brown oil with a decided greenish bloom Deep orange solid.	

Fraction. °C.	Percent.	Characteristics of distillate.	Remarks.
410-430.	.25	Reddish brown oil with green bloom.	
	2.72	Deep orange solid.	Solids some- what waxy.
430-450.	2.70	Deep orange solid.	
450-470.	2.93	Very deep orange solid.	
	27.27	A very porous coke.	
	<u>7.24</u>	Losses.	
	100.00%		

SUMMARY OF RESULTS.

Water, - - - - -	8.21%
Oils and distilled solids, - - - - -	57.28%
Coke or residue, - - - - -	27.27%
Losses in distillation, etc., - - - - -	<u>7.24%</u>
	100.00%

Due to the position of the bulb of the thermometer in the retort, the temperature observed was from 20 to 25 degrees higher than that of the distilling vapor at the time of observation. No correction of this error has been made in the foregoing table.

The calorific value of the coke or residue left from the crude distillation in the copper retort was determined by means of a Parr calorimeter. An average result of three tests gave 15,894 B. T. U. per pound of coke. This shows the heating power above that of the best coals.

The table on the following page gives the results obtained after removing the water from the first distillates and after having subjected the same to three fractional distillations.

A TABLE

SHOWING THE RESULTS OF THREE FRACTIONAL DISTILLATIONS.

Fraction. °C.	Percent.	Kind of distillate.	Color.	Remarks.
70- 75.	.33	Clear oil.	Colorless.	Yellowish
75- 80.	.13	" "	"	tinge after standing for several days
80- 85.	.15	" "	"	"
85- 90.	.10	" "	"	"
90- 95.	.07	" "	"	"
95-100.	.25	" "	"	"
100-105.	.15	" "	"	"
105-110.	.17	" "	"	"
110-115.	.17	" "	"	"
115-120.	.07	" "	"	"
120-125.	.02	" "	"	"
125-130.	.02	" "	"	"
130-135.	.03	" "	"	Oils assume a reddish- yellow tinge
135-140.	.08	" "	"	after stand- ing several days
140-145.	.10	" "	"	"
145-150.	.15	" "	"	"
150-155.	.05	" "	"	"
155-160.	.13	" "	"	"
160-165.	.13	" "	"	"
165-170.	.10	" "	"	"
170-175.	.18	" "	"	"

Fraction. °C.	Percent.	Kind of distillate.	Color.	Remarks.
175-180.	.33	Clear oil.	Colorless.	Oils assume
180-185.	.33	" "	"	- a reddish
185-190.	.35	" "	"	tinge after
190-195.	.50	" "	"	standing for
	.08	White crystalline solid.	White.	several days
195-200.	.40	Clear oil.	Yellowish.	"
	.23	Crystalline solid.	White.	"
200-205.	.68	Clear oil.	Yellowish.	"
	.30	Crystalline solid.	White.	"
205-210.	.50	Clear oil.	Yellowish.	"
	.77	Crystalline solid.	White.	"
210-215.	.52	Clear oil.	Yellow.	"
	1.15	Crystalline solid.	White.	"
215-220.	.48	Clear oil.	Yellow.	"
	2.25	Crystalline solid.	White.	"
220-225.	.23	Clear oil.	Yellow.	"
	2.75	Crystalline solid.	White.	"
225-230.	.10	Clear oil.	Yellow.	"
	1.83	Crystalline solid.	White.	"
230-235.	.10	Clear oil.	Yellow.	"
	1.70	Crystalline solid.	White.	"
235-240.	1.20	Clear oil.	Yellow.	"
	.77	Amorphous solid.	White.	"
240-245.	1.03	Clear oil.	Deep yellow.	Oils dis
	.20	Amorphous solid.	White.	tilling
245-250.	.73	Clear oil.	Deep	above 240°C.
250-255.	.53	" "	yellow	darken upon
			"	exposure.

Fraction. °C.	Percent.	Kind of distillate.	Color.	Remarks.
255-260.	.63	Clear oil.	Deep yellow.	
260-265.	.63	" "	"	
265-270.	.62	" "	"	
270-275.	.67	" "	"	
275-280.	.33	" "	"	
280-285.	.43	" "	"	
	.02	Crystalline solid.	White.	
285-290.	.40	Clear oil.	Deep yellow.	
	.03	Crystalline solid.	White.	
290-295.	.47	Clear oil.	Deep yellow.	
	.10	Crystalline solid.	White.	
295-300.	.37	Clear oil.	Deep yellow.	
	.07	Crystalline solid.	White.	
300-305.	.43	Clear oil.	Deep yellow.	
	.13	Crystalline solid.	Pale yellow.	
305-310.	.43	Clear oil.	Deep yellow.	
	.27	Crystalline solid.	Pale yellow.	
310-315.	.30	Clear oil.	Deep yellow.	
	.37	Crystalline solid.	Pale yellow.	
315-320.	.13	Clear oil.	Deep yellow.	
	.50	Crystalline solid.	Pale yellow.	
320-325.	.07	Clear oil.	Deep yellow.	
	.60	Crystalline solid.	Pale yellow.	
325-330.	.67	Crystalline solid.	Pale yellow.	
330-335.	.60	" "	" "	
335-340.	.77	" "	" "	
340-345.	.97	" "	" "	

Fraction. °C.	Percent.	Kind of distillate.	Color.	Remarks.
345-350.	1.32	Crystalline solid.	* Pale yellow.	
350-355.	.97	" "	" "	
355-360.	.90	" "	" "	
360-365.	.03	Oil.	Deep yellow.	
	1.00	Crystalline solid.	Yellow.	
365-370.	.03	Heavy oil.	Light brown.	
	.87	Crystalline solid.	Yellow.	
370-375.	.23	Heavy oil with bloom.	Brown.	
	.63	Crystalline solid.	Yellow.	
375-380.	.03	Heavy oil with bloom.	Brown.	
	.77	Flaky crystalline solid.	Yellow.	
380-385.	.70	" "	" "	
385-390.	.90	" "	" "	
390-395.	.67	" "	" "	
395-400.	.50	" "	" "	
400-405.	.37	" "	"	Orange yellow.
405-410.	.73	" "	" "	"
410-415.	.67	" "	" "	"
415-420.	.63	" "	" "	"
420-425.	.43	" "	"	Orange.
425-430.	.43	" "	" "	
430-435.	.33	Fine crystalline solid.	Deep orange.	
435-440.	.33	" "	" "	
440-445.	.23	" "	" "	

Fraction. °C.	Percent.	Kind of distillate.	Color.	Remarks.
445-450.	.05	Fine crystalline solid.	Very deep orange.	
450-455.	.13	" " "	"	
455-460.	<u>.10</u>	" " "	"	
	46.91			

SUMMARY OF RESULTS.

Water mechanically removed, - - - - -	8.21%
Distilled oils and solids, - - - - -	46.91%
Residue and losses in distillation, <u>44.88%</u>	
	100.00%

No temperature corrections have been made in the above table. The following table, however, gives the correct bounding temperatures for each fraction as determined by means of the temperature correction curve given on page 20.

A TABLE

OF CORRECTED TEMPERATURES; MELTING POINTS AND SPECIFIC GRAVITIES.

Fraction. Observed °C.	Corrected °C.	Specific gravity. of liquids at 20°C.	Melting points of solids °C.
70- 75.	70.3- 75.4	.8714	
75- 80.	75.4- 80.5	.8722	
80- 85.	80.5- 85.6	.8730	
85- 90.	85.6- 90.7	.8739	
90- 95.	90.7- 95.8	.8745	
95-100.	95.8-100.9	.8754	



Fraction.		Specific gravity of liquids at 20° C.	Melting points of solids °C.
Observed °C.	Corrected °C.		
100-105.	100.9-106.0	.8756	
105-110.	106.0-111.1	.8762	
110-115.	111.1-116.3	.8767	
115-120.	116.3-121.4	.8787	
120-125.	121.4-126.6	.8795	
125-130.	126.6-131.7	.8817	
130-135.	131.7-136.9	.8854	
135-140.	136.9-142.0	.8836	
140-145.	142.0-147.2	.8851	
145-150.	147.2-152.3	.8897	
150-155.	152.3-157.5	.8949	
155-160.	157.5-162.7	.9051	
160-165.	162.7-167.9	.9080	
165-170.	167.9-173.1	.9158	
170-175.	173.1-178.4	.9197	
175-180.	178.4-183.6	.9273	
180-185.	183.6-188.9	.9450	
185-190.	188.9-194.1	.9514	
190-195.	194.1-199.4	.9636	73
195-200.	199.4-204.6	.9652	70
200-205.	204.6-210.0	.9663	55
205-210.	210.0-215.3	.	45



Fraction		Specific gravity of liquids at 20°C.	Melting points of solids °C.
Observed °C.	Corrected °C.		
210-215.	215.3-220.7		53
215-220.	220.7-226.0		66
220-225.	226.0-231.4		54
225-230.	231.4-236.7		53
230-235.	236.7-242.0	1.0185	57
235-240.	242.0-247.2	1.0221	68
240-245.	247.2-252.5	1.0275	69
245-250.	252.5-257.8	1.0281	50
250-255.	257.8-263.1	1.0285	
255-260.	263.1-268.4	1.0289	
260-265.	268.4-273.7	1.0298	
265-270.	273.7-279.0	1.0375	
270-275.	279.0-284.3	1.0442	
275-280.	284.3-289.6	1.0513	
280-285.	289.4-294.9	1.0529	
285-290.	294.9-300.2	1.0591	
290-295.	300.2-305.6	1.0576	
295-300.	305.6-311.0	1.0608	
300-305.	311.0-317.0	1.0625	
305-310.	317.0-323.0	1.0757	
310-315.	323.0-329.0	1.0744	
315-320.	329.0-335.0	1.1297	



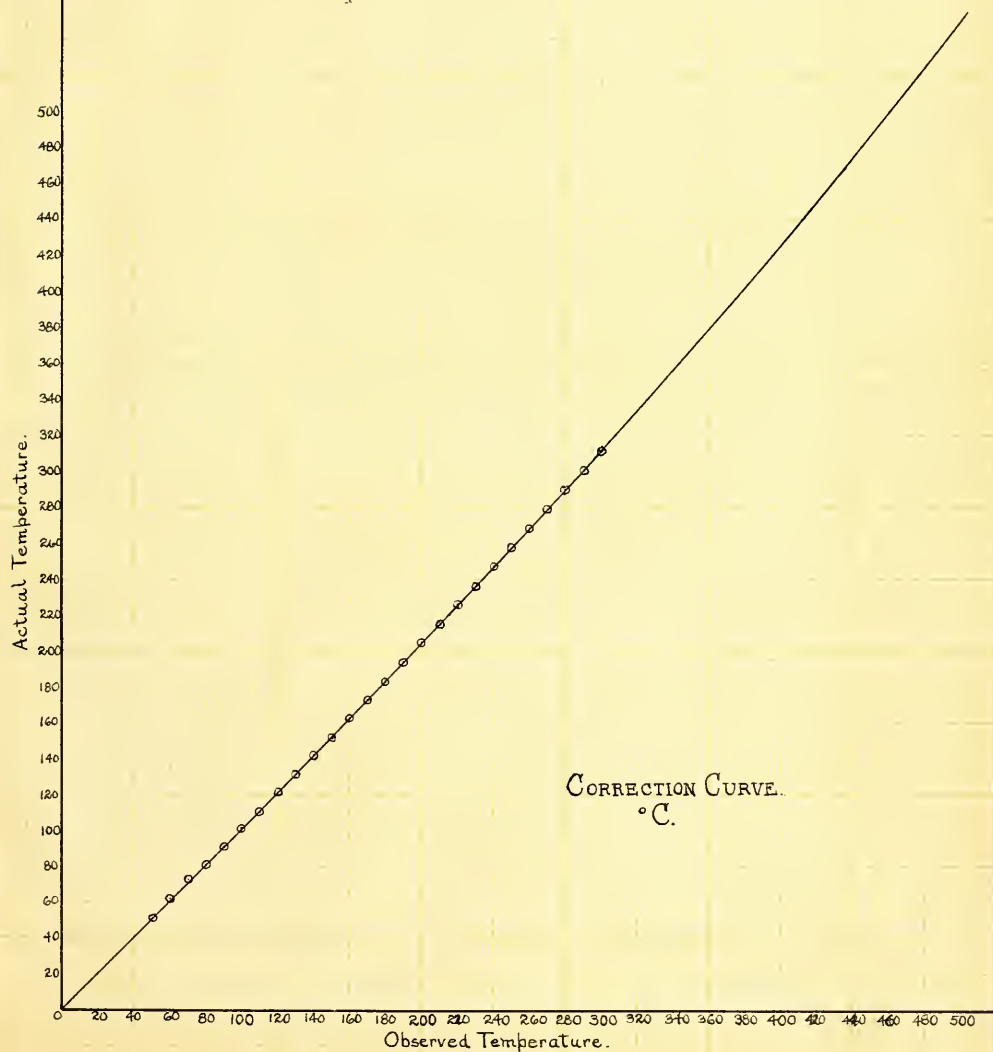
Fraction		Specific gravity of liquids at 20°C.	Melting points of solids °C.
Observed °C.	Corrected °C.		
325-330.	340.0-346.0		102
330-335.	346.0-352.0		107
335-340.	352.0-358.0		106
340-345.	358.0-364.0		103
345-350.	364.0-370.0		98
350-355.	370.0-376.0		95
355-360.	374.0-380		88
360-365.	380.0-386.0		99
365-370.	386.0-392.0		
370-375.	392.0-398.0		
375-380.	398.0-404.0		75
380-385.	404.0-410.0		60
385-390.	410.0-416.0		58
390-395.	416.0-422.0		112
395-400.	422.0-428.0		109
400-405.	436.0-442.0		110
405-410.	436.0-442.0		125
410-415.	442.0-447.0		125
415-420.	447.0-452.0		127
420-425.	452.0-457.0		100
425-430.	457.0-462.0		110
430-435.	462.0-468.0		110

Fraction		Specific gravity of liquids at 20°C.	Melting points of solids °C.
Observed °C.	Corrected °C.		
435-440.	468.0-474.0		108
440-445.	474.0-480.0		108
445-450.	480.0-486.0		115
450-455.	486.0-492.0		120
455-460.	492.0-498.0		125

Owing to the incomplete separation of the various constituents due to insufficient fractional distillation, chemical tests were not of much value. From the physical tests employed, it is quite probable that naphthalene is present to the extent of possibly 10%. If this is the case, additional value is attached to water gas tar, as naphthalene is the direct or indirect basis for innumerable dyes.

Naphthalene when treated with nitric acid, yields nitro-naphthalene which upon oxidation gives nitrophthalic acid. By reducing this, we get amido-naphthalene which when oxidized yields phthalic acid. Phthalic acid upon treatment with an excess of lime yields the benzene basis for coal tar dyes. Naphthalene, itself, is the basis for a very large number of dyes. Its chief use in the dye industry is in the production of oxy-azo dyes which form one of the most important classes of dyes. They are noted for their brilliancy and tendency to be fast colors.





Assuming that naphthalene is present in the water gas tar to the extent of 10% and that it sells at the rate of 5 cents per pound, we find that a ton of the crude tar contains close to \$10. worth of naphthalene. At present, the crude tar is bought from the gas works by manufacturers of roofing materials at the rate of 2 cents per gallon or \$4.80 per ton.

From calorific tests of the crude water gas tar by means of the Parr calorimeter, the heating power was found to lie between 20,400 and 20,600 B. T. U. per pound of fuel or tar. Assuming a good coal to run about 15,000 B. T. U. per pound, we find that with coal at prices above \$3.60 and with the cost of firing with coal or tar the same, it is more advantageous to use tar as a fuel. The coke, as has been mentioned before, has a high calorific value, namely, 15,900 and is more than equivalent to a good coal in the pulverized state. This retort coke might be advantageously used in the cement and other industries where pulverized coal is now being burnt.

At the present writing, it seems that about the only use to which water gas tar is put, is for the preparation of roofing materials. One of the manufacturers of roofing paper in Chicago, subject the crude water gas tar to distillation. The fraction from ordinary temperature up to 360°F. is called light oils and is mixed with pitch and higher fractions to form a black, waterproof varnish. The distillate coming over between 360°F. and 500°F. is

known as "creosote oil" and is used in the preparation of roofing papers, etc.. Between 500° F. and 600° F., the heavy oils come over and these are used for fuel and as a constituent of varnish. The residue in the retort is a soft pitch having a specific gravity of 1.2235 at 20° C. The pitch is used as a roofing tar.

In conclusion, it may be said that while the results of the present investigation have been rather limited and perhaps valueless, it is hoped by those who undertook this work, that their results and data may be a help to others working in this field of research.





